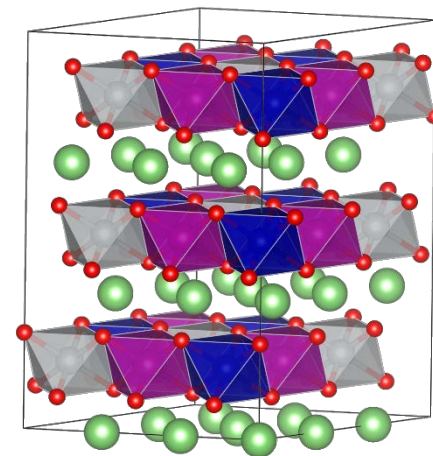# ENABLING HIGH-ENERGY/ VOLTAGE LITHIUM-ION CELLS: THEORY AND MODELING

ES253

HAKIM IDDIR

2017 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

OVERVIEW

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 65%

Budget

- Total project funding:
  – FY16 - $4000K
- ES252, ES253, and ES254

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  – Cost, Performance, and Safety

Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

PROJECT OBJECTIVES - RELEVANCE

Objectives:

Atomistic modeling to help provide fundamental understanding and prediction of $Li(Ni_{1-x-y}Mn_xCo_y)O_2$ (NMC) bulk and surface structures, processes at surfaces and interfaces, and electrolyte-surface interactions to address the problems associated with "enabling" high-energy lithium-ion cells.

Approach:

Perform first-principles density functional theory (DFT) at the GGA+U and the (HSE06) hybrid functional levels. Computational cells including up to several hundred atoms in the periodic unit are employed. This work is being coordinated with experimental efforts, including the synthesis and characterization groups.
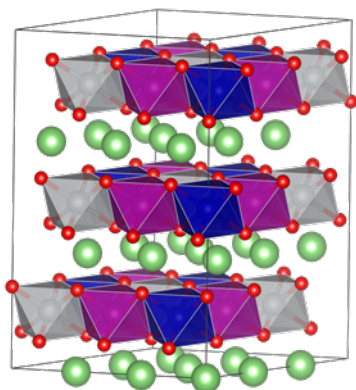
Milestones:

- Theoretical predictions of the low-energy surfaces of NMC particles and the effect of nickel content on particle shape surface reconstructions and elemental segregation
- Theoretical predictions of electrolyte- and additive-NMC surface interactions.
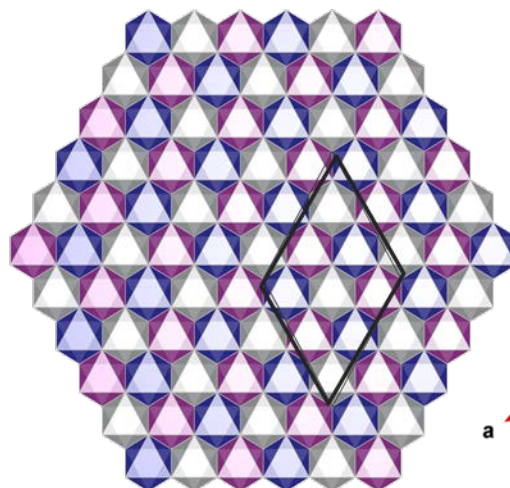
H.I. and J. G. AMR June 5-9, 2017

See also ES254

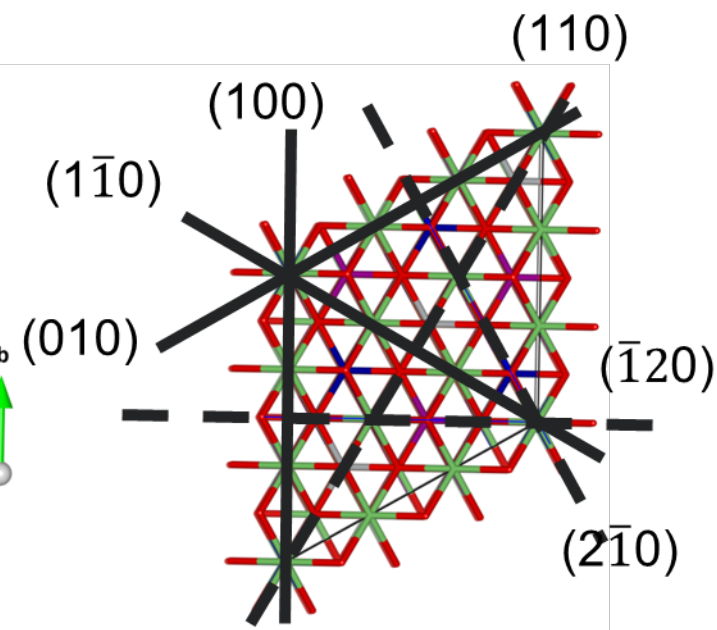# Low energy surfaces of NMC 111

NMC111 unit cell

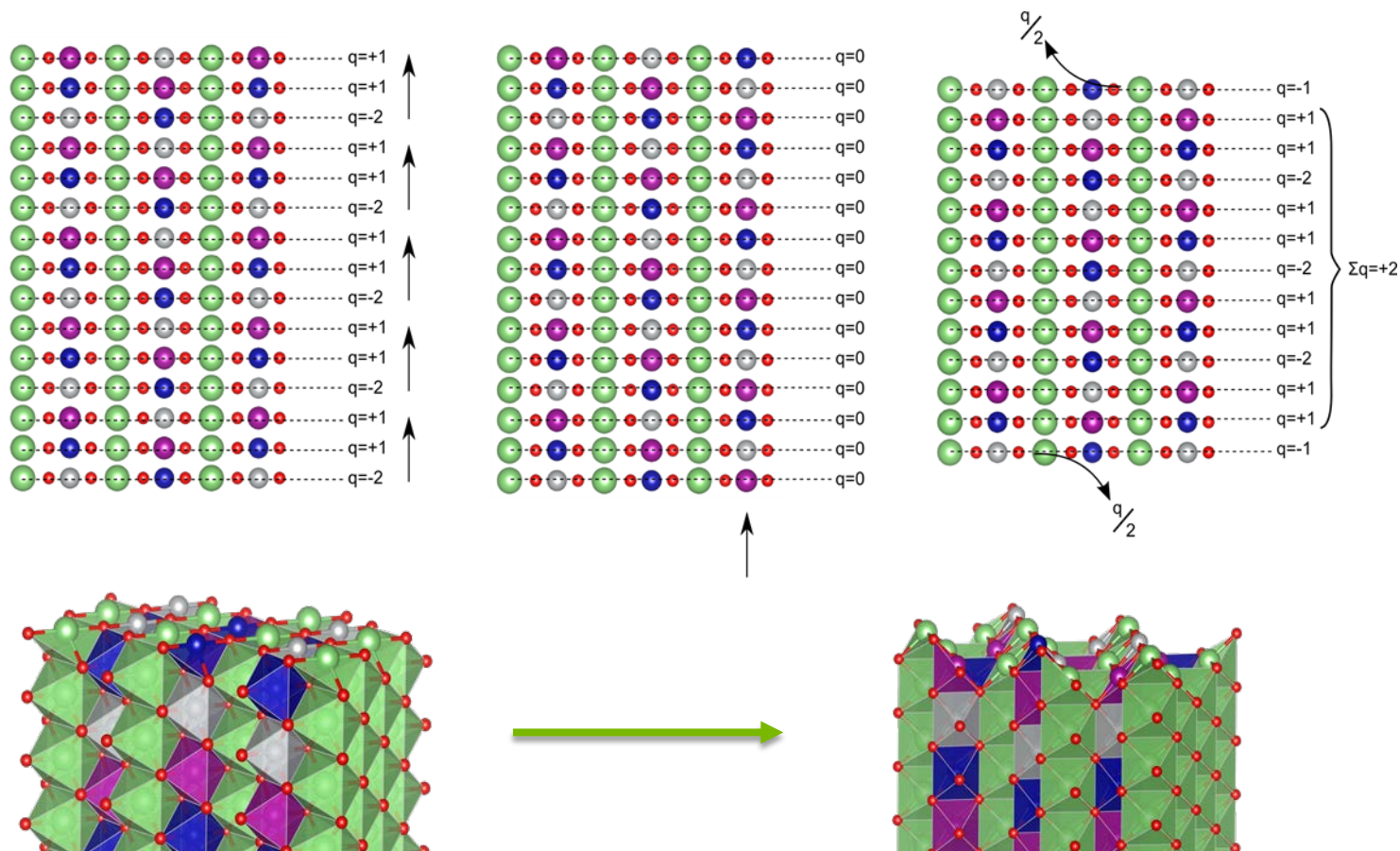Transition metal layer configuration

Example families of equivalent planes

- NMC111 composition has a well defined configuration of the transition metal layer
- The surface energies of low Miller-index families are needed to construct the equilibrium particle shape.

Dipole Free Surface Models

- Supercell models with periodic boundary conditions were used
- Periodic boundary conditions require zero net dipole

# Surface Energies for Low Miller Index Families of NMC111 Surfaces

| surface orientation	surface termination	surface energy (J/m²)
(104)	Ni, Mn, Co, O	0.76
(001)	Ni, Mn, Co, O	0.89
(110)$_A$	Ni, Mn, Co, O	1.32
(110)$_B$	Co, O	1.67
	Ni, O	1.77
	Mn, O	1.88
(012)	Ni, Mn, Co, O	1.97
(100)	Ni, Mn, Co, O	2.27
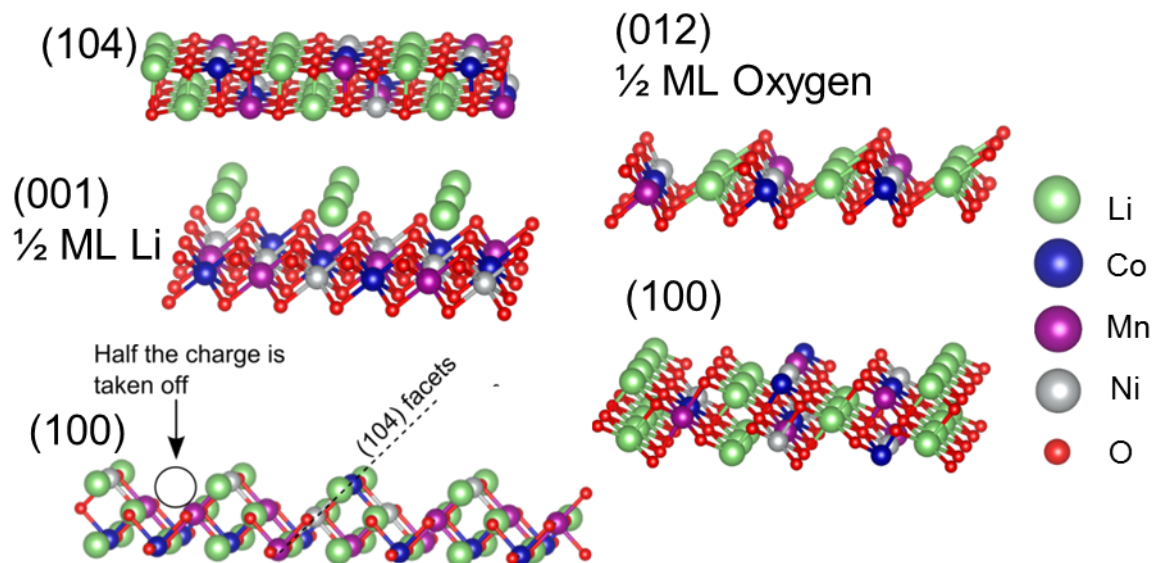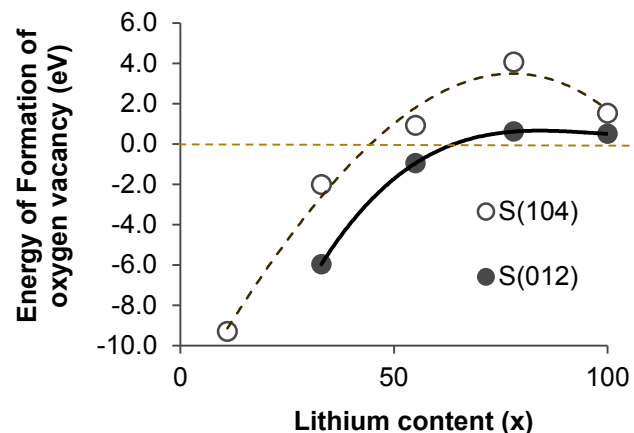
- The trend in surface energy can be rationalized by counting the broken bonds when the surface is cleaved.
- The lower the lithium content (high SOC, high voltage), the easier it is to reduce the surface.
- For lithium contents below ~40% (60% SOC), the release of oxygen from the (104) surface becomes a spontaneous process.
- For the (012) surface this process becomes spontaneous for lithium contents below 60% (40% SOC).

(104)

(001) ½ ML Li

(100)

Half the charge is taken off

(100) (104) facets

(012) ½ ML Oxygen

(100)

Li
Co
Mn
Ni
O

Thermodynamic analysis of polar surfaces

Surface energy of (012) facet as a function of the oxygen chemical potential
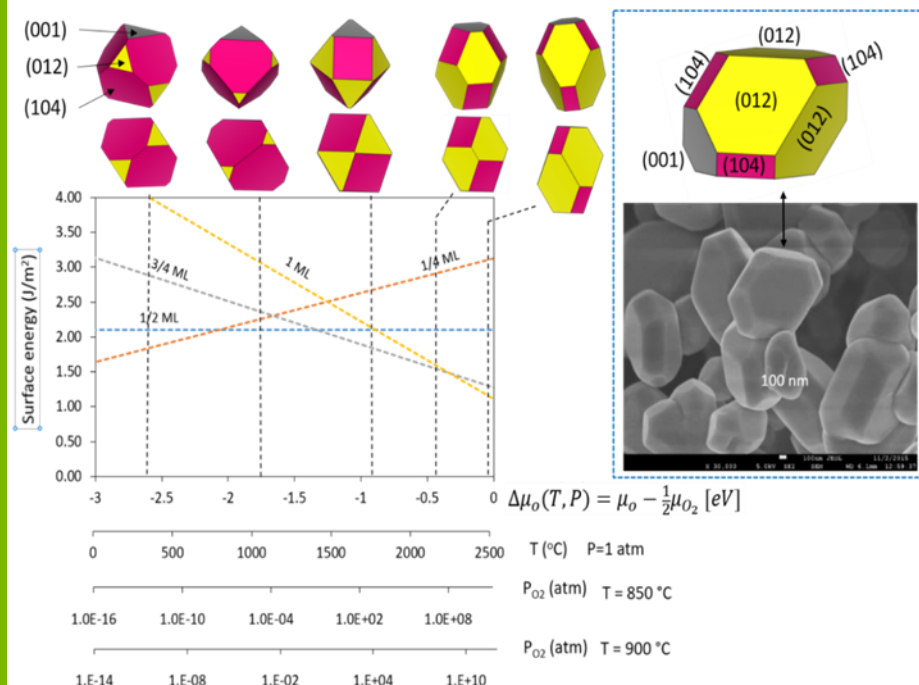
Surface energy of the (001) facet as a function of the Li chemical potential

$$\Delta\mu_o(T,P) = \mu_o - \frac{1}{2}\mu_{O_2} \ [eV]$$

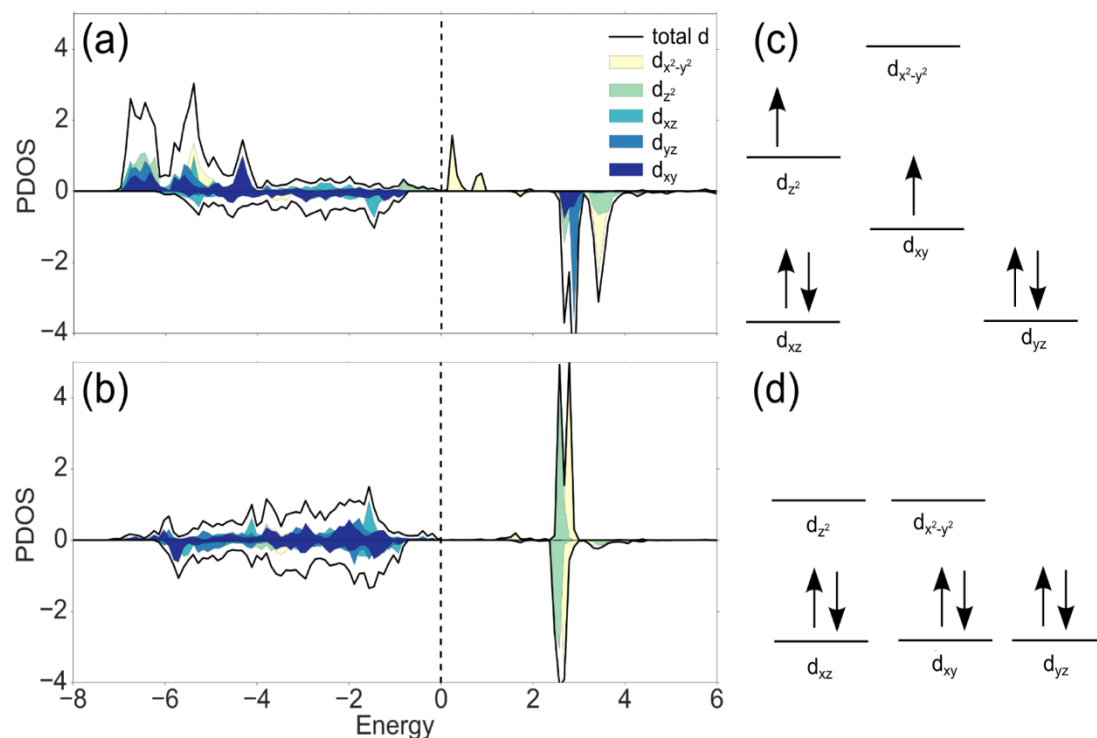$$\mu_{Li}(T,P) = \mu_{Li}^o - \mu_{Li-metal}$$

$$\mu_{Li} \sim -2.5 eV$$
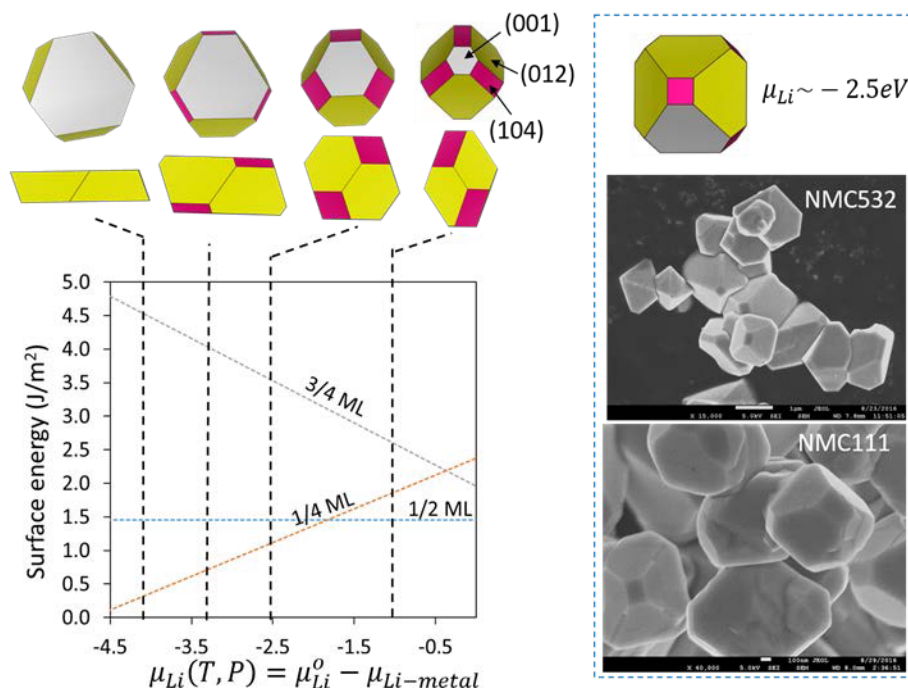
The crystal particle shape from the Wulff construction is shown at select conditions indicated by the dotted lines. An SEM image of the synthesized particle is also shown.

Calculations predict the crystal shape of NMC for high O chemical potential and low Li chemical potential.

Co Spin State

Co PDOS d-orbitals. (a) Co in the surface layer of the slab. (b) Co in the bulk region of the slab. (c) Surface layer Co d orbital electronic configuration schematic. (d) Bulk Co d orbital electronic configuration schematic.

- **Bulk:** unoccupied states and the magnetization is zero, indicating Co^{3+} in the low spin configuration.

- This configuration is consistent with the d band splitting caused by an octahedral coordination.

- The crystal field splitting energy is less than the spin pairing energy (P). Hence, the low spin configuration is favored.

- **Surface:** magnetization, Bader charges, and PDOS analysis indicates Co^{3+} in an intermediate spin state.

- The crystal field splitting energy is < P

Oxygen vacancy formation energy

Surface	Coordination	Oxygen vacancy formation energy (eV)
(104)	Co - axial	5.4
	Ni - axial	2.2
	Mn - axial	1.5
(012)	Co, Ni - equatorial	1.9
	Co, Mn – equatorial	1.1
	Mn, Ni - equatorial	0.6

$$Mn^{4+} + e^- \rightarrow Mn^{3+}$$

For the fully lithiated surface Mn^{4+} is more susceptible to be reduced than is Co^{3+} or Ni^{2+}. Therefore, when an oxygen atom is removed, the easiest charge transfer pathway goes through the Mn ion. The reduction of Mn, weakens its bonding to oxygen.
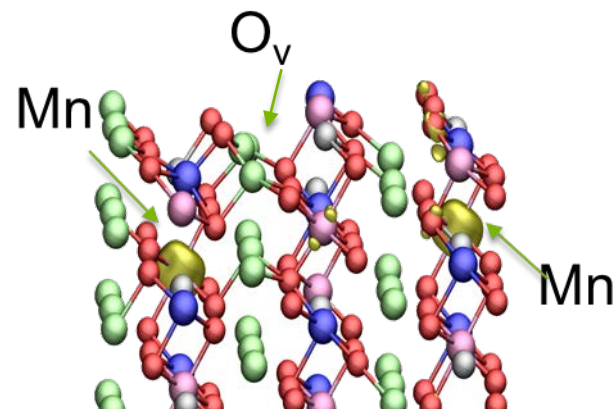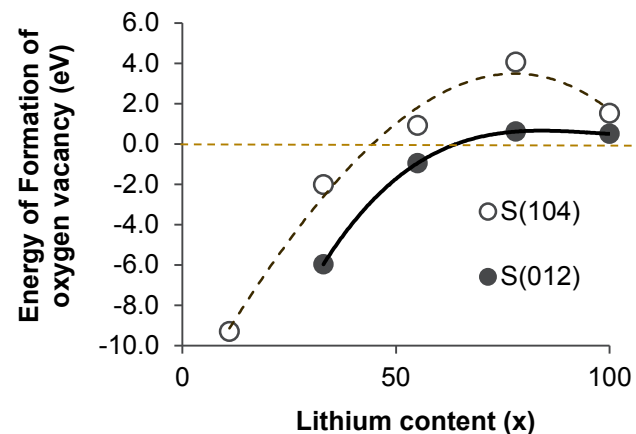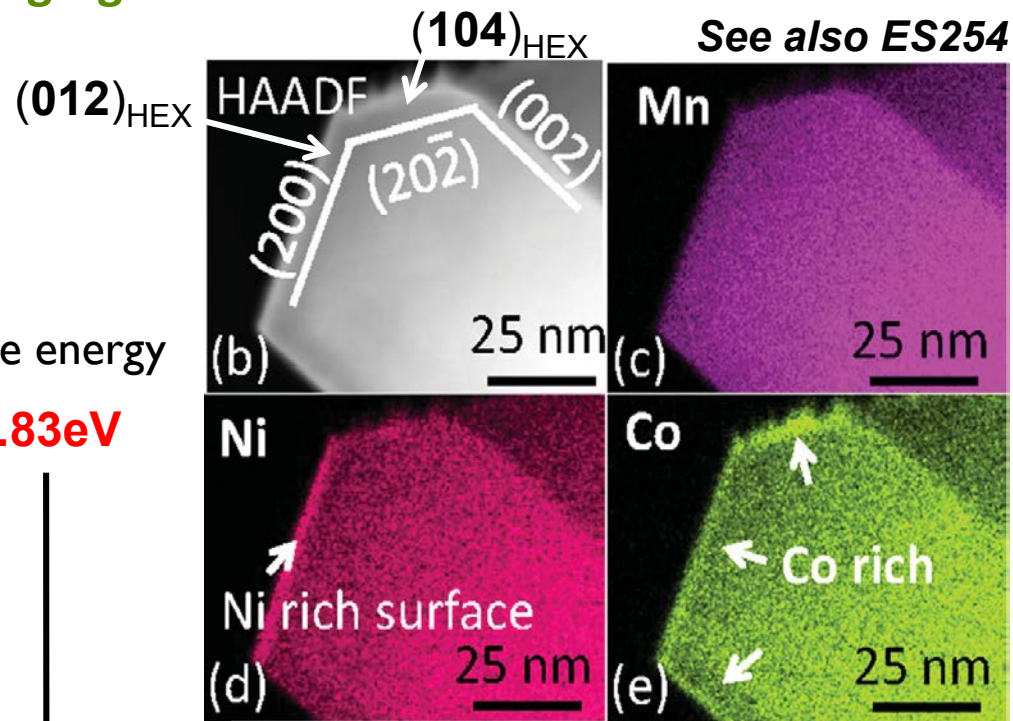
9

The stability of Co ions at the surface produces a thermodynamic driving force for segregation
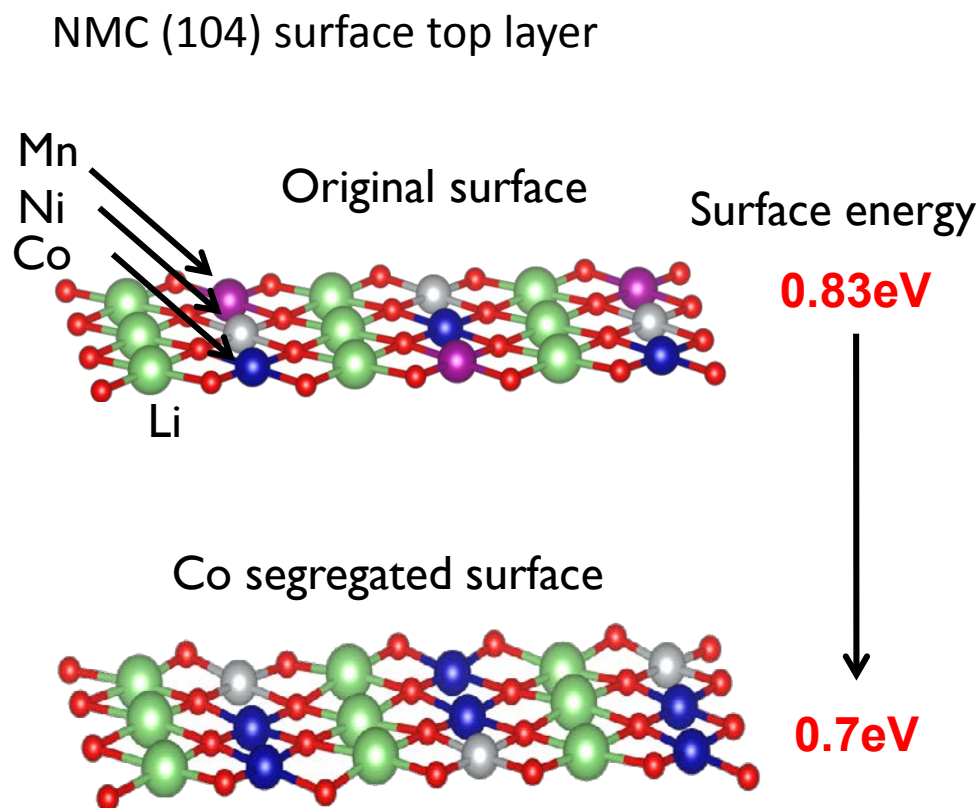
EDS mapping on one
$Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ particle

See also ES254

NMC (104) surface top layer

Mn
Ni
Co

Original surface

Li

Surface energy

0.83eV

Co segregated surface

0.7eV

$(012)_{HEX}$ $(104)_{HEX}$

Source:
Yan, P.; Zheng, J.; Zheng, J.; Wang, Z.; Teng, G.; Kuppan, S.; Xiao, J.; Chen, G.; Pan, F.; Zhang, J.-G.; Wang, C.-M. "Ni and Co Segregations on Selective Surface Facets and Rational Design of Layered Lithium Transition-Metal Oxide Cathodes". *Adv. Energy Mater.* **2016**, *6* (9), 1502455.

TM segregation

$\Delta E_{104} = -0.12eV$

$\Delta E_{104} = -0.08eV$

$\Delta E_{012} = 3.92eV$

$\Delta E_{012} = 2.11eV$

Co rich

Co rich

(104)　(012)
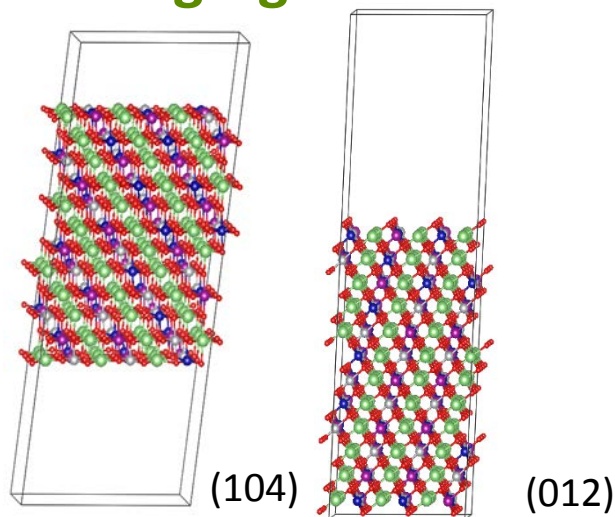
$\Delta E = E_{baseline} - E_{segregated}$

$\Delta E_{104} = 5.83eV$

$\Delta E_{104} = 5.44eV$

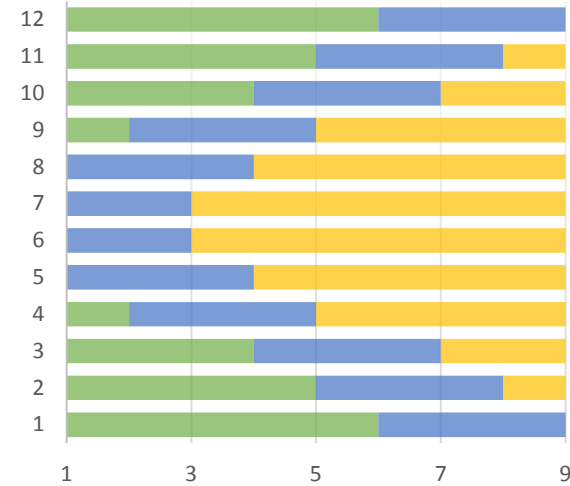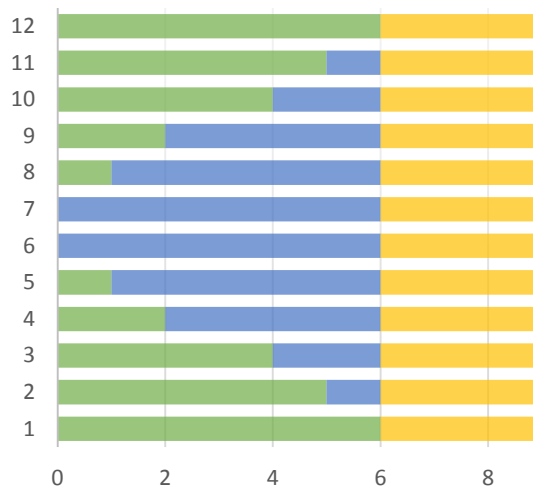$\Delta E_{012} = 2.31eV$

$\Delta E_{012} = 2.54eV$

Ni rich

Mn rich

- The stability of Co ions at the surface produces a thermodynamic driving force for surface segregation
- For (104) surface top layer Co:Mn, Co:Ni
- For (012) segregation is not favorable. The second lowest energy is Co:Ni rich
- DFT+U preliminary data (work in progress)
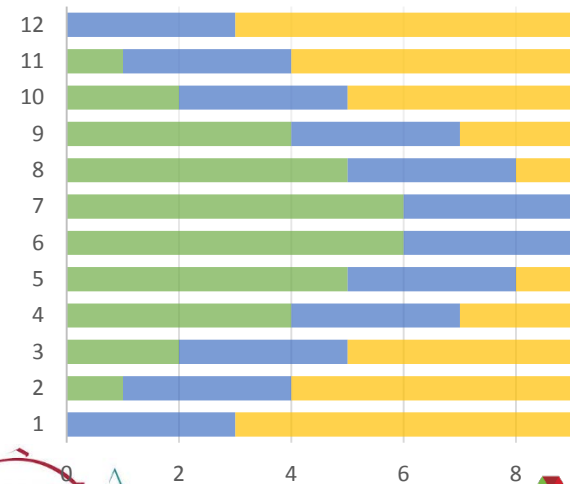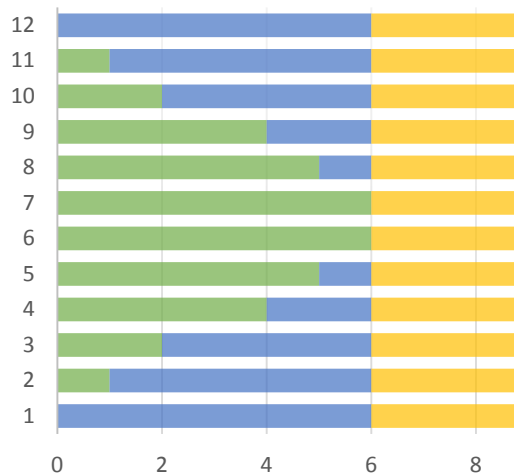
TMSPi + HF reaction is thermodynamically favorable
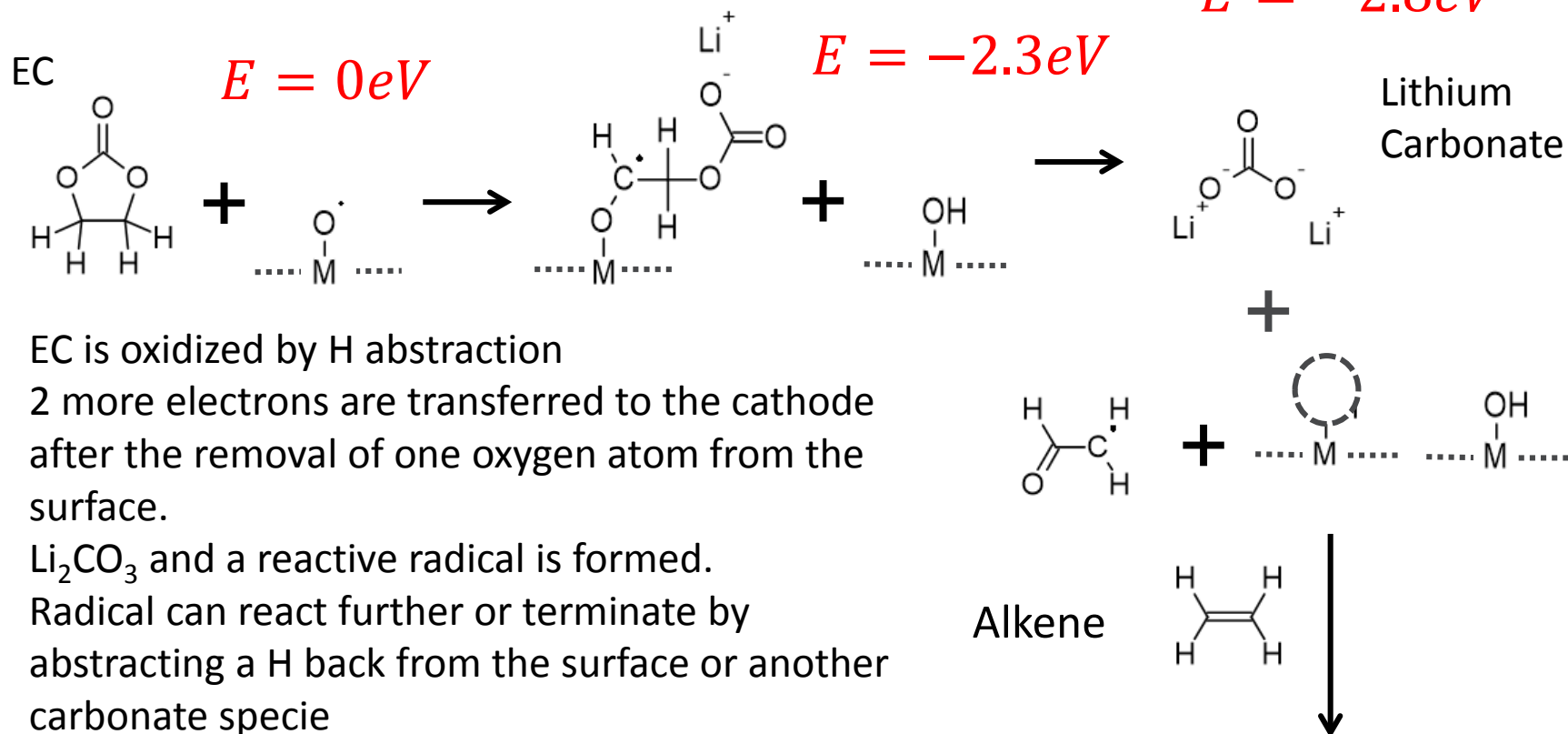

R-1

R-2

R-3

equilibrium
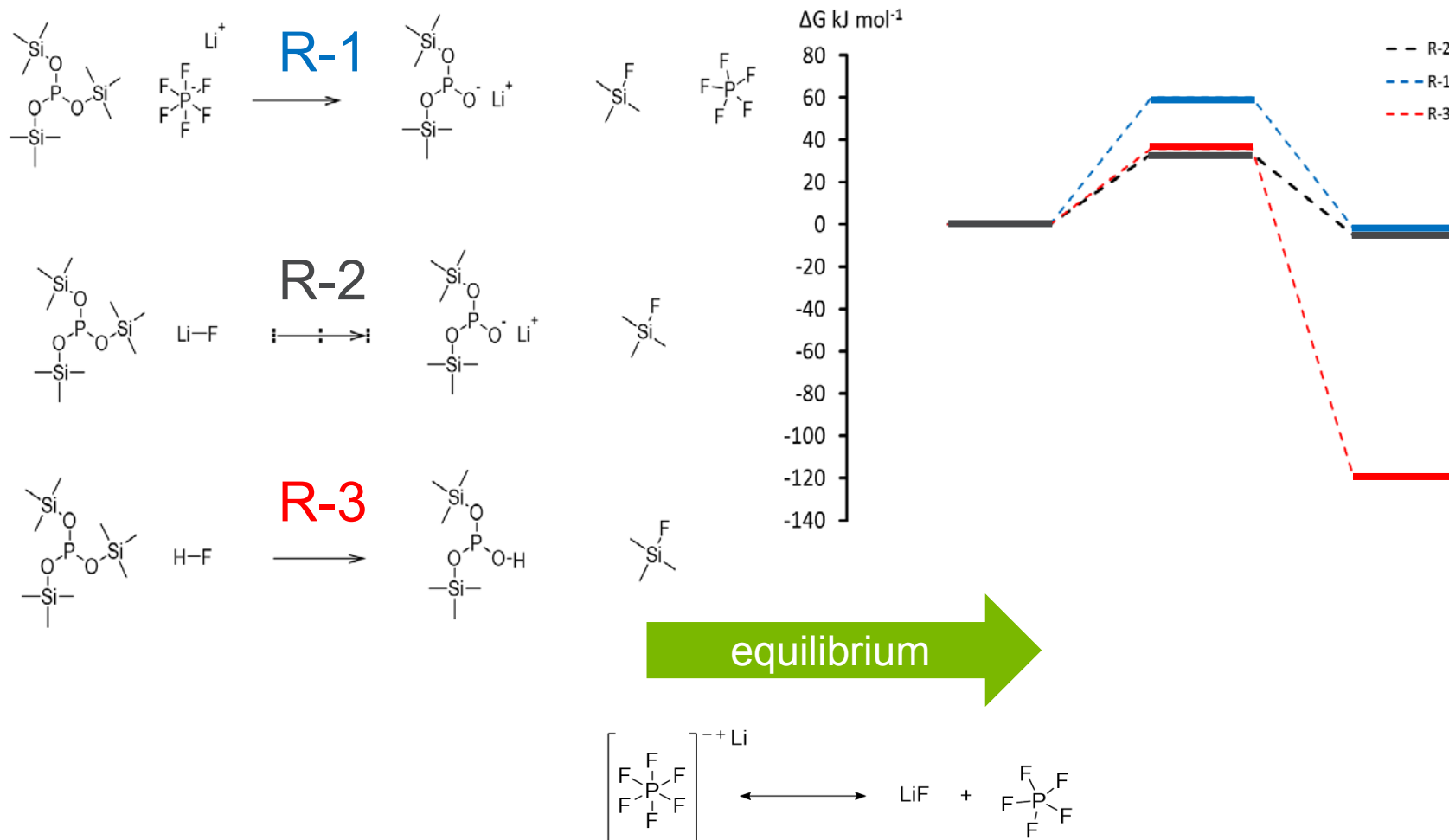
TMSPi reaction with HF
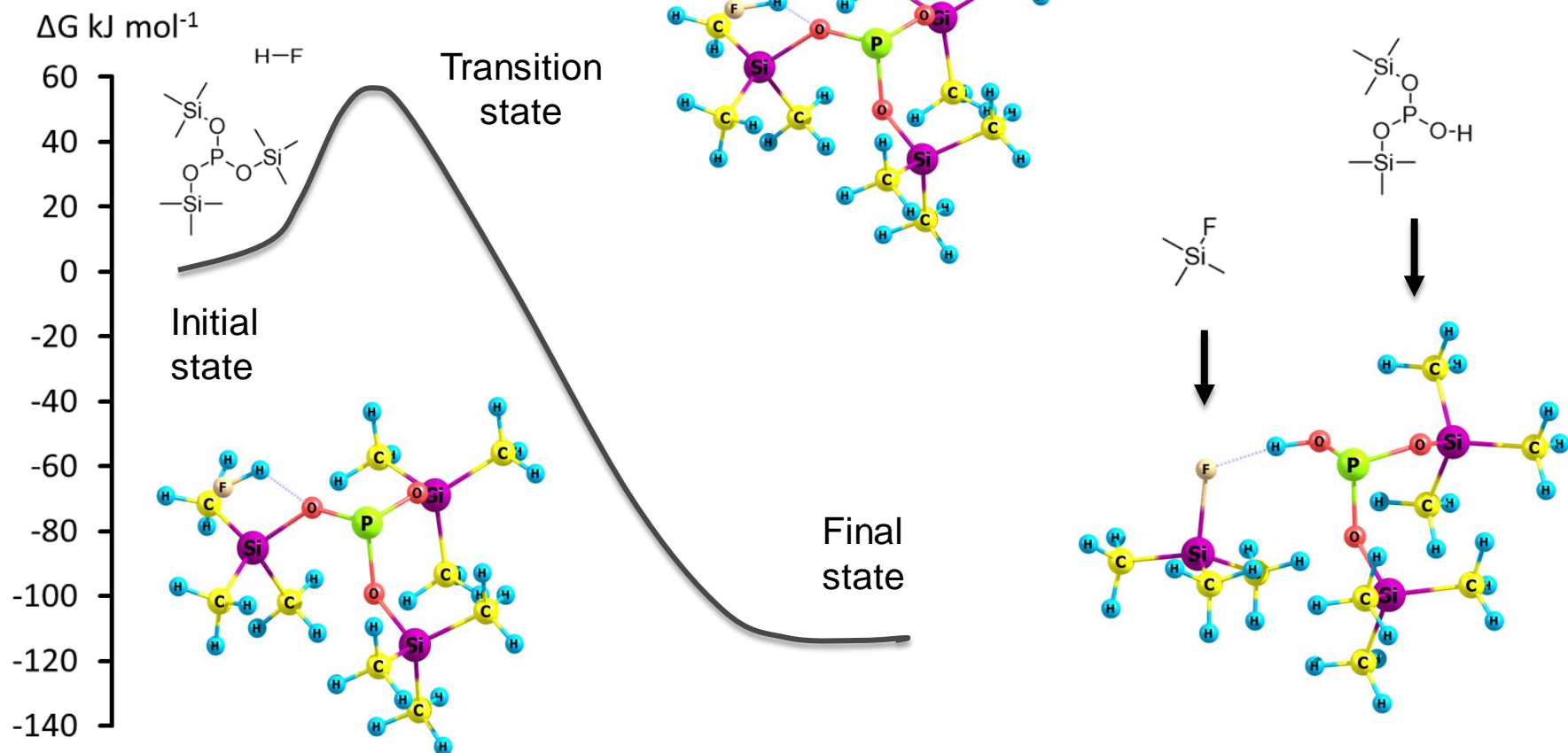
→ The reaction is thermodynamically favorable
→ The energy barrier is ~45kJ/mol

Electrolyte - cathode surfaces interaction

EC oxidation

EC

$$E = 0eV$$

$$E = -2.3eV$$

$$E = -2.8eV$$

Lithium Carbonate

- EC is oxidized by H abstraction
- 2 more electrons are transferred to the cathode after the removal of one oxygen atom from the surface.
- Li_2CO_3 and a reactive radical is formed.
- Radical can react further or terminate by abstracting a H back from the surface or another carbonate specie

Alkene

$$E = -3.3eV$$

$$E = -3eV$$

Aldehyde
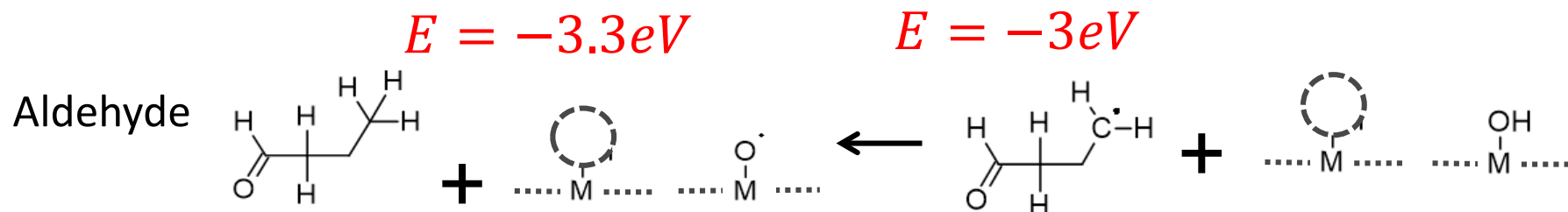
Electrolyte - cathode surfaces interaction

EMC oxidation

$$E = 0eV$$

$$E = -0.56eV$$

Alkene

$$E = -0.9eV$$

EMC
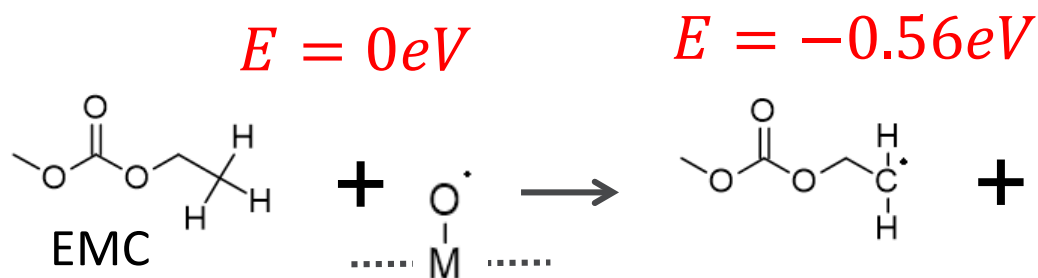
- EMC is oxidized by H abstraction.
- It is not thermodynamically favorable to take of an oxygen from the surface.
- The formed radical could react with other species. For example alkene (shown in shaded area), EC, EMC…
- The radical could take the H back form the surface or another EC or EMC molecule.

→ EC is more reactive with the surface than EMC

Alkyl carbonate
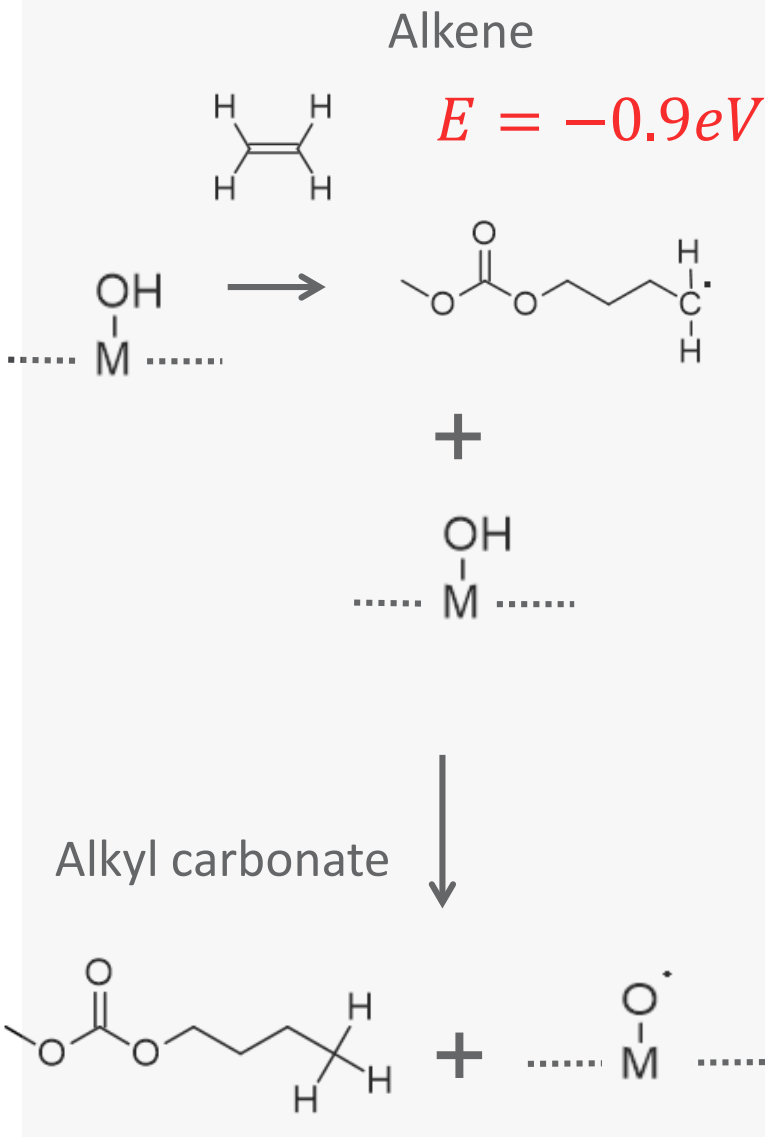
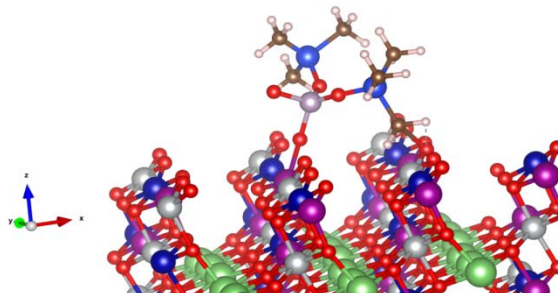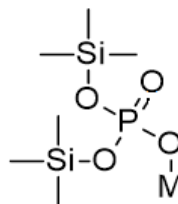# Additives - Cathode surface interactions

- TMSPi interaction with the surface is weak due to bulky TMS groups

- TMSPi can lose a TMS group and form a phosphate at the surface
- The phosphate absorbs favorably at the surface

- Li_2PO_4 is very stable absorbed on the oxygen atoms of the (012) surface

$$E_{ads} = -0.08eV$$
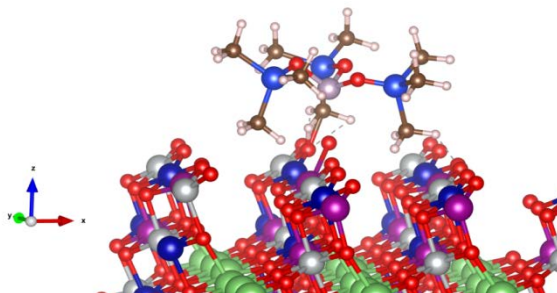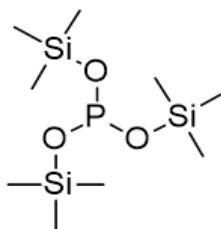
$$E_{ads} = -1.2eV$$

$$E_{ads} = -1.9eV$$
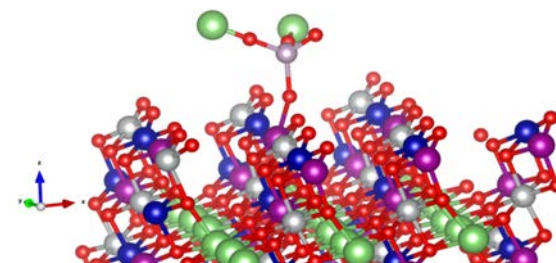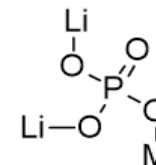
Increasing Stability

Additives - Cathode surfaces interaction

- TEPi is oxidized to TEPa at the surface.
- H abstraction on the surface is under study.
- No stable species at the surface.

- After absorption at the surface Mn^{4+} is reduced.
- The creation of an oxygen vacancy at the surface of fully lithiated cathode is favorable near Mn

$$\Delta E = -3.6 eV$$
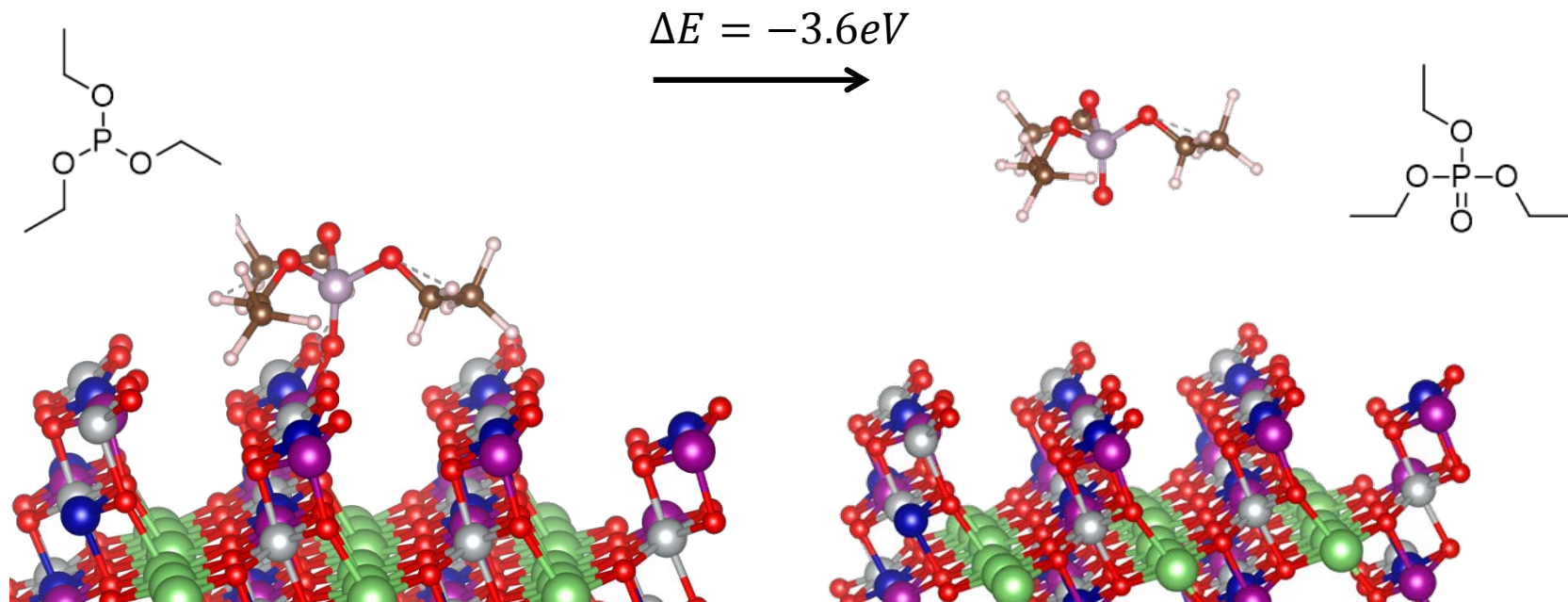
TEPi + NMC surface → TEPa + reduced NMC surface

Additives - Cathode surfaces interaction

TTFP CH_2CF_3 groups are less bulky than TMS groups in TMSPi.
The molecule is easily oxidized to TMSPa

If TTFP loses a CH_2CF_3 groups the product is stable at the surface.

$$E_{ads} = -1.28 eV$$

$$\Delta E = -3.1 eV$$

Increasing Stability

OAK RIDGE National Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Argonne NATIONAL LABORATORY
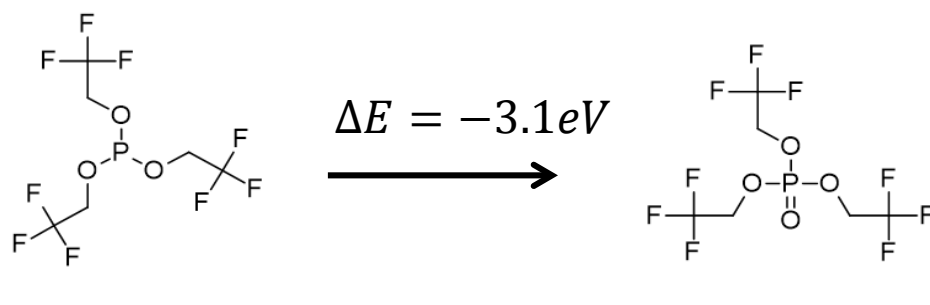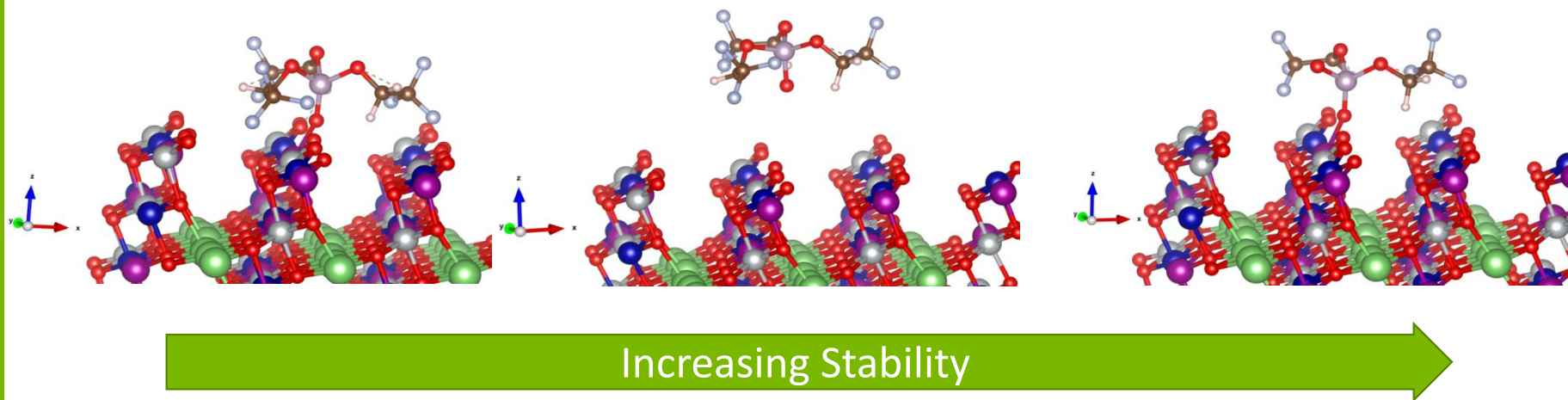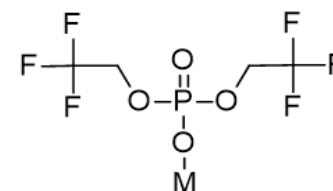
Additives - Cathode surfaces interaction
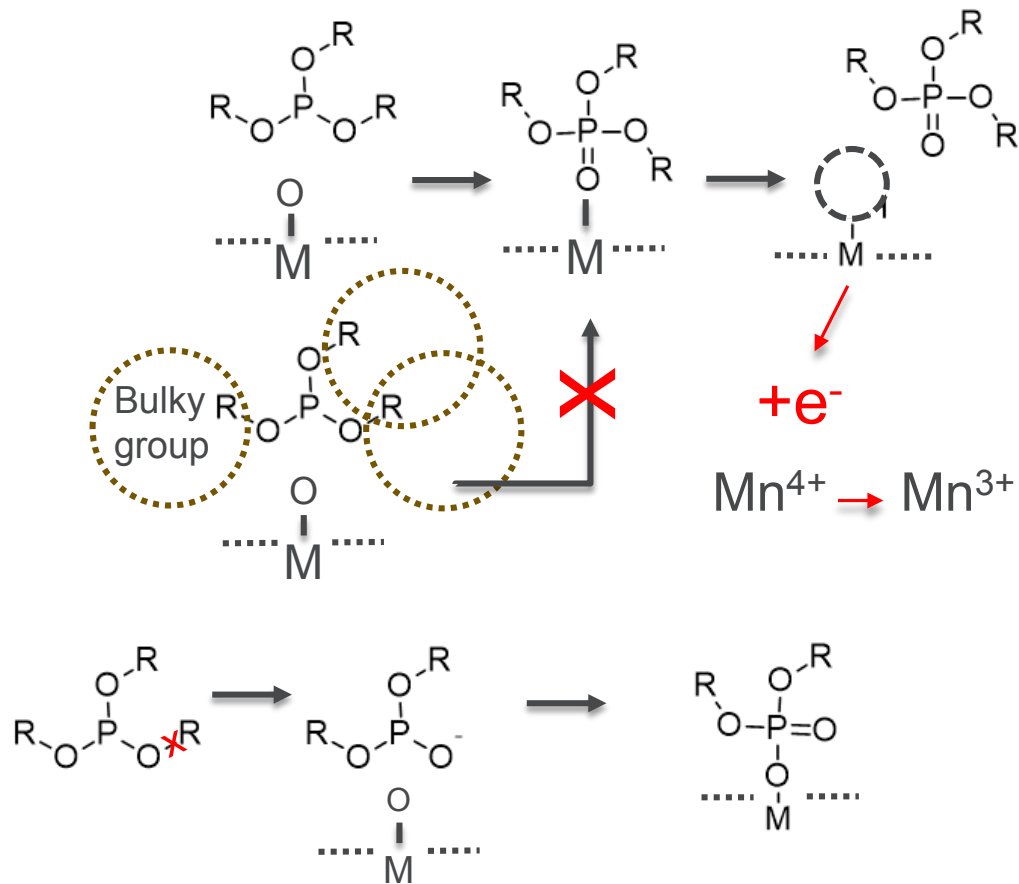
- Phosphite can be oxidized to phosphate by taking one oxygen off the cathode surface. Unless, steric effects impede the P-O interaction (path indicated by **X**)

- Chemical reactions in the electrolyte can lead to stable phosphate on the surface

- Mn^{4+} is reduced to Mn^{3+} when a molecule is oxidized on the surface of fully lithiated NMC111

Experimental evidence consistent with TTFP breakage and oxidation after 60 hour hold at 4.6 V

XPS suggests *TTFP* attached to NMC532 surface is missing one CF_3 group
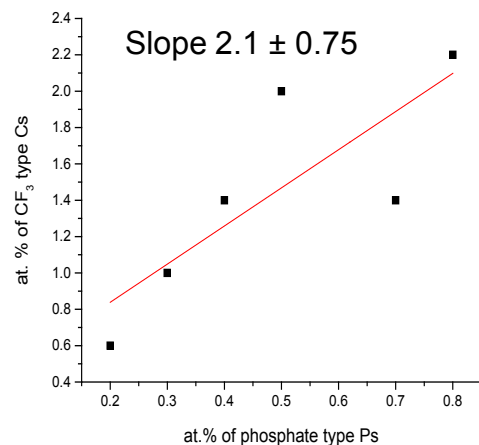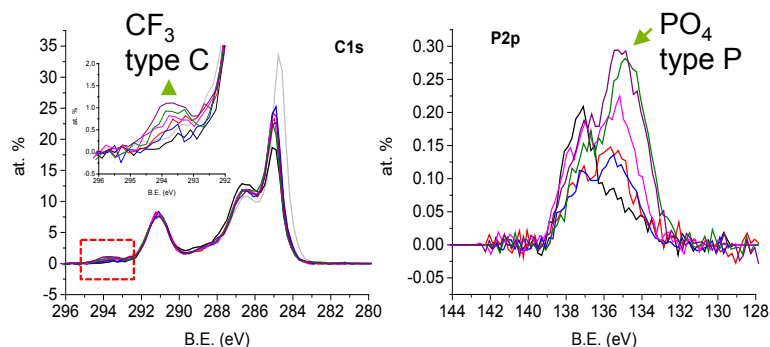
TTFPa derivatives detected in electrolyte by HPLC-ESI-MS

M.W. 276

M.W. 290

M.W. 262
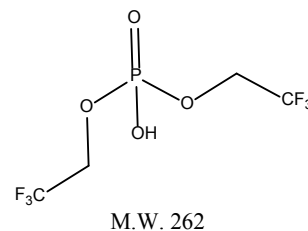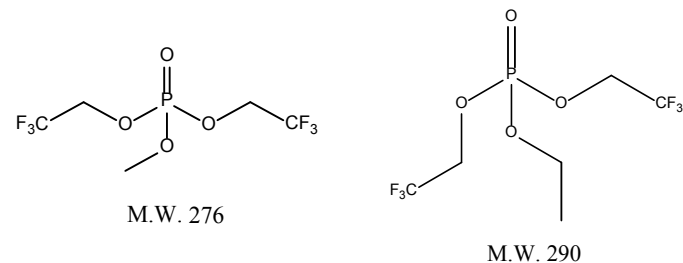
Mass/charge (m/z) of ion detected	Observed isotopic ratio	Expected isotopic ratio
263.0	5.5	4.6
277.0	5.3	5.7
291.0	7.4	6.8

Data provided by Argonne Post-Test Characterization Facility

ELECTROCHEMICAL MODELING

BATTERY MODEL IN GPROMS INCORPORATING THE POTENTIOSTATIC HOLD AND PARASITIC SIDE REACTION

Porous electrode theory, concentrated solution theory
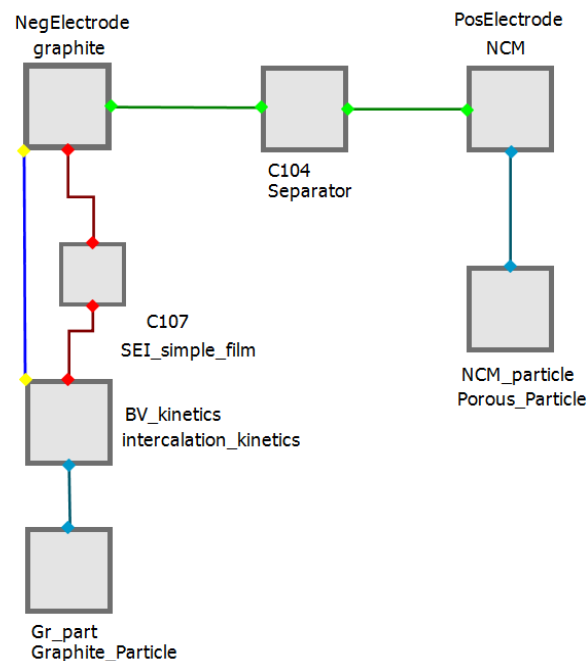
Potentiostatic hold value (4.6 V)

model ramps up voltage to hold value
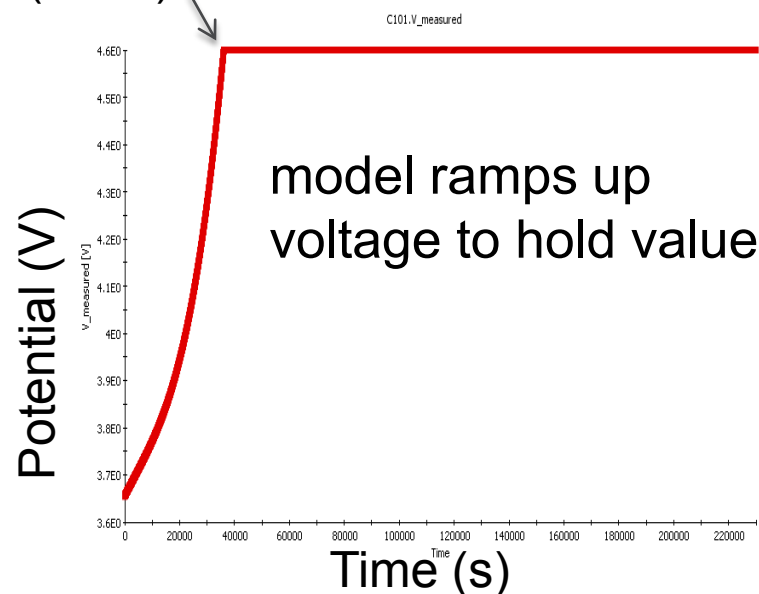
Nicole R. Vadivel, Seungbum Ha, Meinan He, Dennis Dees, Steve Trask, Bryant Polzin, and Kevin G. Gallagher, Journal of The Electrochemical Society, **164** (2) A508-A517 (2017)

TAFEL EQUATION FIT TO SIDE REACTION

need to determine experimentally

$$i = i_0 \exp\left(\frac{\alpha F}{RT}[\eta]\right)$$

measured
current

overpotential,
set variable

DETERMINING THE ARRHENIUS FIT OF THE EXCHANGE CURRENT DENSITY (I_0)
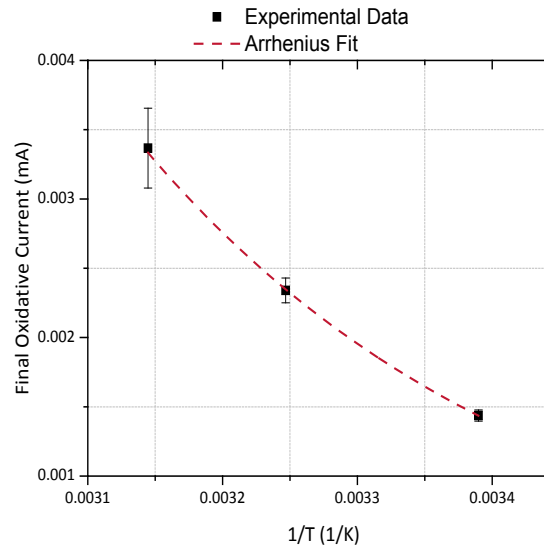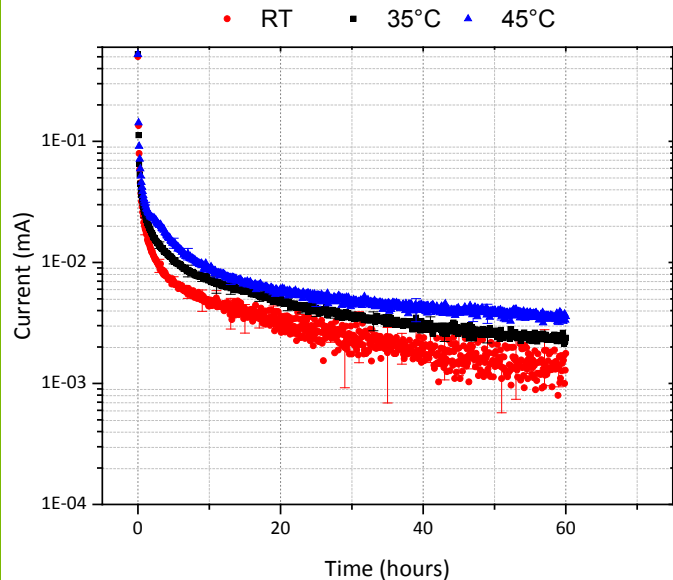
$$i_0 = a \exp\left(b\,\frac{1}{T}\right)$$

Fitting Parameter	Value	Standard Error
a	164.28	21.25
b	-3436.0	38.87

$$i_0 = i_{0,\,ref}\exp\left(-\frac{E_a}{RT}\right) \qquad E_a = 28567\,\frac{\text{J}}{\text{mol}}$$

TAFEL EXPRESSION WITH LOW TRANSFER COEFFICIENTS FITS EXPERIMENTAL DATA
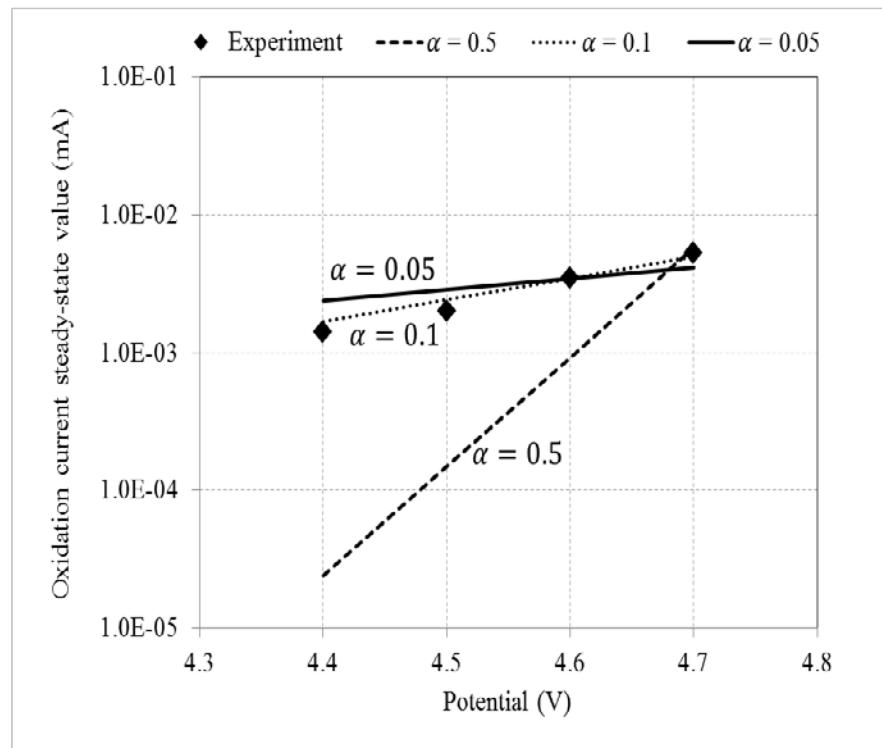
Tafel expression:

$$i = i_0 \exp\left(\frac{\alpha F}{RT}[\eta]\right)$$

PARASITIC SIDE REACTION CURRENT INCREASES WITH INCREASING POTENTIAL HOLD VALUE

Full Cell Simulation of Current Change as a Function of Potential Hold Value

$\alpha = 0.05$

Legend:
- 4.4 V
- 4.5 V
- 4.6 V
- 4.7 V

Y-axis: Current Density (mA)
X-axis: Time (hours)
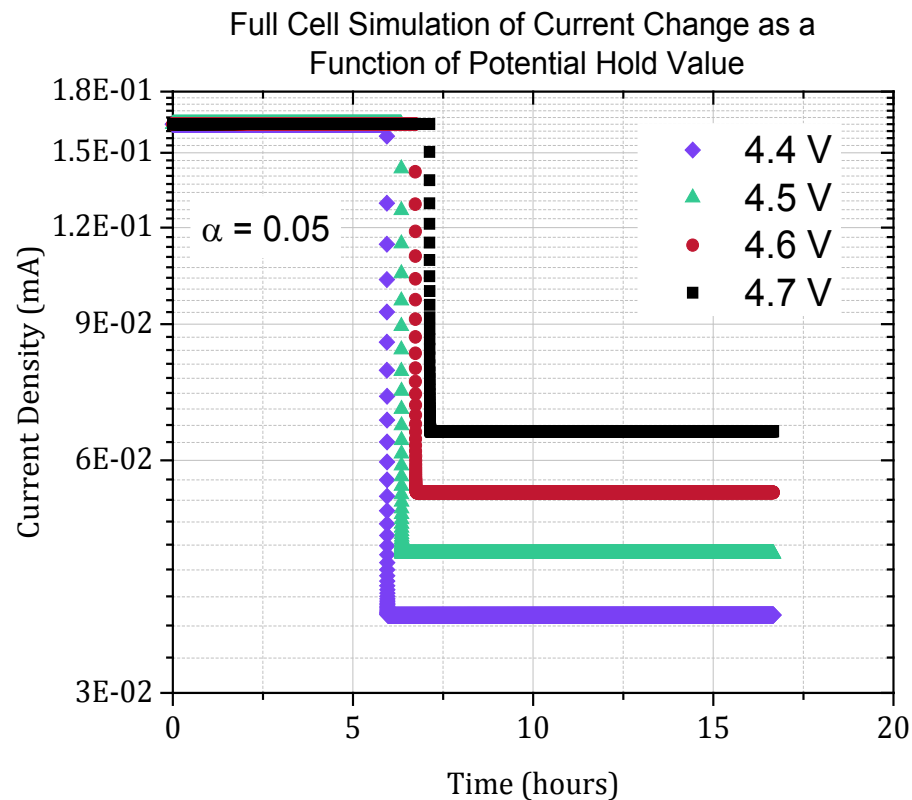
Matches experimental trends

26

SUMMARY

- A reliable model was built for Li-ion NMC based cathode materials which allowed predicting the surface structures, relative stability, and particle shapes.

- The electronic structure of NMC cathode material was analyzed giving a deeper understanding of the material's properties.

- The interaction between typical electrolyte molecules and NMC cathode surfaces was modeled leading to the proposal of a decomposition pathway.

- The mechanism of action of phosphite-based electrolyte additives was defined leading to possible improvement and design of new additives.

- The driving force for transition metals segregation to the surface in NMC particles was determined.

- A spin-atom cluster expansion methodology (Collaboration with Eunseok Lee from the University of Alabama and Roy Benedek from CSE-ANL) was developed.

- Electrochemical modeling work showed that cross-talk between the electrodes is the primary contribution to the observed leakage current after the relaxation of concentration gradients has ceased.

FUTURE WORK – REST OF FY 2017

- Continue modeling transition metal segregation

- Continue modeling surface coatings and reconstructions

- Continue electrolyte-additive/NMC surfaces interaction studies

- Continue to support the development of new methods to help in modeling Ni-rich NMC materials and disseminate results in publications

Any proposed future work is subject to change based on funding levels

H.I. and J.G. AMR June 5-9, 2017

PUBLICATIONS AND PRESENTATIONS

Publications

- Juan C. Garcia, Javier G. Bareno, Jianhua Yan, Guoying Chen, Andrew Hauser, Jason R Croy, and Hakim Iddir, "Surface Structure, Morphology and Stability of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ Cathode Material", The Journal of Physical Chemistry C: DOI: 10.1021/acs.jpcc.7b00896

- Eunseok Lee, Hakim Iddir, and Roy Benedek, "Rapidly convergent cluster expansion and application to lithium ion battery materials", Phys. Rev. B 95, 085134 (2017)

- Roy Benedek and Hakim Iddir, "Simulation of First-Charge Oxygen-Dimerization and Mn-Migration in Li-Rich Layered Oxides xLi_2MnO_3-$LiMO_2$ and Implications for Voltage Fade", The Journal of Physical Chemistry C: 121, 6492 (2017): DOI: 10.1021/acs.jpcc.7b00277

- C. Peebles, R. Sahore, J.A. Gilbert, J.C. Garcia, A. Tornheim, J. Bareño, H. Iddir, C. Liao, D.P. Abraham, " Tris(trimethylsilyl) phosphite (TMSPi) and triethyl phosphite (TEPi) as electrolyte additives for lithium ion batteries: mechanistic insights into differences during $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$-graphite full cell cycling", J. Electrochem. Soc. 164 (2017) *under review*.

- I. Bloom, R. Sahore, C. Peebles, D.P. Abraham, J. Gilbert, "Effect of Additives on the Performance of High-Voltage, NMC-based Cells: A Combinatorial Approach", J. Electrochem. Soc. 164 (2017) *under review*.

Presentations

- Juan Garcia. ANL 2016 Postdoctoral Research and Career Symposium. "Morphology and stability of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ surfaces", Argonne National Laboratory
- Garcia J. C., Bareño J., Yan J., Chen G., Hauser A., Croy J. R., Iddir H. "Structure, morphology and stability of layered $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ surfaces", APS March Meeting 2017, New Orleans, LA.
- Hakim Iddir, "Atomistic Models of High-capacity Layered Metal Oxide Cathode Materials", Argonne National Laboratory. February 16th, 2017 (invited talk) . AIChE Chicago February 2017 Meeting and Tour.
- Hakim Iddir, Condensed Matter/Biological Physics Seminar UIC. March 9, 2017 (invited talk), "Atomistic models of high-capacity layered metal oxide cathode materials"

See also ES252, ES254

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)

High-Energy/Voltage Project Contributors

- Daniel Abraham
- Mahalingam Balasubramanian
- Chunmei Ban
- Javier Bareno
- Roy Benedek
- Ira Bloom
- Guoying Chen
- Jason Croy
- Lamuel David
- Dennis Dees
- Fulya Dogan Key
- Nancy Dudney
- Alison Dunlop
- Juan Garcia
- Kevin Gallagher
- James Gilbert
- Binghong Han
- Meinan He
- Katherine Hurst

- Hakim Iddir
- Brian Ingram
- Manar Ishwait
- Andrew Jansen
- Christopher Johnson
- Ozge Kahvecioglu Feridun
- Kaushik Kalaga
- Andrew Kercher
- Robert Klie
- Michael Kras
- Gregory Krumdick
- Eunseok Lee
- Jianlin Li
- Xuemin Li
- Chen Liao
- Wenquan Lu
- Anil Mane
- Chengyu Mao
- Jagjit Nanda

- Daniel O'Hanlon
- Cameron Peebles
- Bryant Polzin
- Nicole Raley Vadivel
- Yang Ren
- Ritu Sahore
- Youngho Shin
- Ilya Shkrob
- Xin Su
- Robert Tenent
- Rose Ruther
- Adam Tornheim
- Stephen Trask
- John Vaughey
- Gabriel Veith
- David Wood
- Jianhua Yan
- Pierre Yao
- Zhengcheng Zhang